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Crystal Structure, Electron Spin Resonance, and Magnetic Exchange Coupling in Bis(μ -chloro)bis[cyclopentadienyl(triethylphosphane)vanadium(II)]

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rather than true disorder. Hydrogen isotropic temperature factors were estimated on the basis of the thermal motion of the associated carbons. After all shift:sd ratios were less than 0.3, convergence was reached. No unusually high correlations were noted between any of the variables in the last cycle of least-squares refinement, and the final difference density map showed no peaks greater than $0.25 \text{ e}/\text{\AA}^3$. The atomic scattering factors for the non-hydrogen atoms were computed from numerical Hartree-Fock wave functions;¹⁴ for hydrogen those of Stewart, Davidson, and Simpson¹⁵ were used. The anomalous dispersion coefficients of Cromer and Liberman¹⁶ were used for Ru. All calculations were made by using Molecular Structure Corp. TEXRAY 230 modifications of the

SDP-PLUS series of programs. The data collection and processing parameters are outlined in Table VII, and the positional parameters and their standard deviations are included in Table VIII.

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Supplementary Material Available: Tables pertinent to the X-ray crystallographic determination of **4d** including bond lengths, bond angles, refined and general temperature factor expressions, least-squares planes, and calculated hydrogen fractional coordinates (8 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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Crystal Structure, Electron Spin Resonance, and Magnetic Exchange Coupling in Bis(μ -chloro)bis[cyclopentadienyl(triethylphosphane)vanadium(II)]

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The X-ray structure and magnetic characterization (ESR, susceptibility) of the dinuclear vanadium(II) compound $[\text{CpVCl}(\text{PEt}_3)]_2$ are described. The title compound crystallizes in the monoclinic space group as purple-red crystals, with cell dimensions of $a = 12.760$ (5) \AA , $b = 12.616$ (7) \AA , $c = 17.707$ (7) \AA , and $\beta = 102.32$ (3) $^\circ$, in space group $P2_1/c$, with $Z = 4$. The structure was solved by using Mo $K\alpha$ radiation ($\lambda = 0.71073$ \AA) and 7090 reflections (3607 unique intensities, 1390 of which were considered as observed), resulting in $R(F) = 0.0589$ ($R_w(F) = 0.0458$). The structure consists of roof-shaped dinuclear V_2Cl_2 units and terminal η^5 -cyclopentadienyl and triethylphosphane ligands. The V-V distance amounts to 3.245 (3) \AA . The bridge, though roof-shaped (dihedral angle of 132.9°), is quite symmetric as deduced from V-Cl distances of 2.438 (3) and 2.440 (3) \AA . The dimeric unit results in antiferromagnetic interaction between the two V(II) (d^3) ions, as seen from ESR spectra and magnetic susceptibility studies at low temperature.

Introduction

The chemistry of vanadium(II) is poorly developed,^{2,3} and only a relatively small number of coordination compounds have been described in great detail by X-ray structure analysis. Apart from coordination compounds of the type $\text{V}(\text{ligand})_6\text{X}_2$ and $\text{V}(\text{ligand})_4\text{X}_2$ (X = halide; L = (heterocyclic) nitrogen donor ligand),⁴ vanadium(II) Tutton salts,⁵ and cationic dinuclear V(II) complexes, $[\text{V}_2(\mu\text{-X})_3(\text{THF})_6]^+$,⁶ mostly organometallic V(II) species have been described,⁷ often by using THF salts as intermediates. In earlier studies⁶⁻⁸ it turned out that cyclopentadienyl V(III) compounds of formula $\text{CpVX}_2(\text{L})_2$ (L = phosphane-type ligand; X = Cl, Br) are easily reduced to species analyzing as $\text{CpVCl}(\text{L})$. Extensive characterization by a variety of physical methods in solution strongly indicates that these species are dimeric in nature with halogen-bridged dinuclear species, just as has been reported before⁶ for $[\text{V}_2\text{X}_3(\text{THF})_6]^+$ species.

The present paper describes the characterization of one of these compounds by X-ray methods, as well as a study of the dinuclear

Table I. Crystal and Diffraction Data for $[\text{CpVCl}(\text{PEt}_3)]_2$

empirical formula	$\text{C}_{22}\text{H}_{40}\text{Cl}_2\text{P}_3\text{V}_2$
color	purple red
cryst dimens, mm	$0.22 \times 0.15 \times 0.10$
space group	$P2_1/c$
cell dimens (at 25 $^\circ\text{C}$; 24 reflctns; $12^\circ < \theta < 15^\circ$)	
a , \AA	12.760 (5)
b , \AA	12.616 (7)
c , \AA	17.707 (7)
β , deg	102.32 (3)
θ values, deg	$4 < \theta < 44$
molecules/cell	4
V , \AA^3	2784.8
d_{calc} g/cm ³	1.284
wavelength Mo $K\alpha_1$, \AA	0.71073
M_r	539.30
linear abs coeff, cm^{-1}	9.65
total no. of reflcns collcd	7090
no. of unique intens	3607 ($R_{\text{int}} = 0.058$)
final residuals	
$R(F)$	0.0589
$R_w(F)$ ($w = 1/\sigma^2(F)$)	0.0458
goodness of fit for the last cycle(s)	1.75
max Δ/σ for the last cycle	<0.1

species by means of ESR spectroscopy and magnetic susceptibility measurements.

Experimental Section

The compounds studied are extremely air sensitive, and experiments were carried out under rigorously anhydrous and oxygen-free conditions. Solvents (toluene, ether, pentane) were distilled under nitrogen from sodium/potassium melts before use. The compound $[\text{CpVCl}(\text{PEt}_3)]_2$ was prepared as reported before.⁷

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Table II. Fractional Atomic Coordinates^a ($\times 10^4$) for [CpVCl(PEt₃)₂]₂ with Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$)

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B(iso)</i> ^b
V(1)	6481 (1)	4192 (1)	7113 (1)	422 (5)
V(2)	8221 (1)	6039 (1)	7025 (1)	426 (5)
Cl(1)	6504 (2)	6078 (2)	7419 (1)	488 (9)
Cl(2)	8429 (2)	4227 (2)	7537 (1)	413 (8)
P(1)	6148 (2)	3629 (2)	8401 (2)	469 (9)
P(2)	9315 (2)	6775 (2)	8261 (2)	410 (9)
C(1)	5727 (9)	4269 (8)	5853 (6)	100 (5) ^c
C(2)	6457 (9)	3510 (8)	5942 (6)	89 (5)
C(3)	6150 (8)	2763 (8)	6346 (6)	76 (4)
C(4)	5192 (8)	3030 (8)	6548 (6)	76 (4) ^c
C(5)	4942 (8)	3986 (9)	6212 (6)	102 (5)
C(6)	8329 (9)	5773 (8)	5791 (6)	104 (5) ^c
C(7)	7611 (9)	6542 (8)	5769 (6)	89 (5) ^c
C(8)	8120 (8)	7373 (9)	6164 (6)	81 (4)
C(9)	9170 (8)	7108 (8)	6394 (6)	76 (5)
C(10)	9282 (9)	6131 (8)	6147 (6)	87 (5)
C(11)	4766 (7)	3634 (7)	8533 (7)	87 (5) ^c
C(12)	4268 (8)	4692 (9)	8286 (7)	137 (7)
C(13)	6414 (7)	2207 (7)	8653 (6)	74 (4)
C(14)	7506 (8)	1865 (8)	8661 (7)	105 (6)
C(15)	6859 (7)	4354 (5)	9228 (4)	68 (4)
C(16A)	6518 (15)	5399 (6)	9545 (7)	112 (11) ^c
C(16B)	6644 (15)	4141 (8)	10031 (5)	76 (9) ^c
C(17)	10766 (6)	6655 (6)	8324 (6)	52 (3)
C(18)	11148 (7)	5521 (6)	8271 (6)	76 (4)
C(19)	9214 (7)	8178 (6)	8417 (6)	65 (4)
C(20)	8119 (8)	8548 (7)	8450 (7)	97 (5)
C(21)	9095 (7)	6204 (7)	9136 (5)	55 (4)
C(22)	9828 (8)	6524 (7)	9868 (5)	84 (5)

^a Estimated standard deviations in the least significant digits are given in parentheses. ^b *B(iso)* is defined as $\frac{1}{3}\pi^2(\text{trace } \bar{u})$. ^c These atoms show a high thermal anisotropy.

ESR spectra were obtained at X-band and Q-band frequencies from samples of powdered material or frozen toluene solution by using Varian E3, E4, and Q-band instruments. Magnetic susceptibility measurements (4–300 K) were performed on powdered samples by using a Faraday type system (Oxford Instruments) equipped with a Mettler ME 21 electronic vacuum microbalance.

Crystallographic Study of [CpVCl(PEt₃)₂]₂

Dark red crystals were grown by temperature-programmed cooling (0.5 °C/h) of an ether solution from room temperature to –20 °C. The highly air-sensitive crystal was mounted in a glass capillary by using a glovebox with an inert N₂ atmosphere. Intensity data were collected on a Nonius CAD-4 computer-controlled diffractometer by using graphite-monochromated Mo K α radiation. Lattice constants were determined by a least-squares refinement of the angular settings of 24 reflections with $12^\circ < \theta < 15^\circ$. Crystal parameters and information about the data set collected ($4^\circ \leq 2\theta \leq 44^\circ$) are summarized in Table I. The structure was solved by direct methods⁹ (MULTAN78) and Fourier techniques and was refined in full-matrix least-squares refinement cycles, which revealed all non-hydrogen atoms and nine of the 40 hydrogen atoms. These remaining hydrogen atoms were added at a fixed distance of 1 Å. One of the phosphane carbon atoms, viz. C(16), was found disordered and was refined in two positions A and B with 50% probability each. No absorption correction was applied. The final *R* value was 0.0589 for 1390 significant reflections. Atomic positions of the non-hydrogen atoms are listed in Table II. Listings of *F*_o and *F*_c values, hydrogen atom positions, and the thermal parameters of the non-hydrogen atoms are available.¹⁰ Scattering factors including anomalous dispersion were taken from ref 11.

Results and Discussion

Description of the Structure of [CpV(μ-Cl)(PEt₃)₂]₂. The results of the X-ray diffraction study of [CpV(μ-Cl)(PEt₃)₂]₂ are presented in Tables III (distances) and IV (bond angles). Figure 1 shows the molecular structure, illustrating the dimeric nature of the

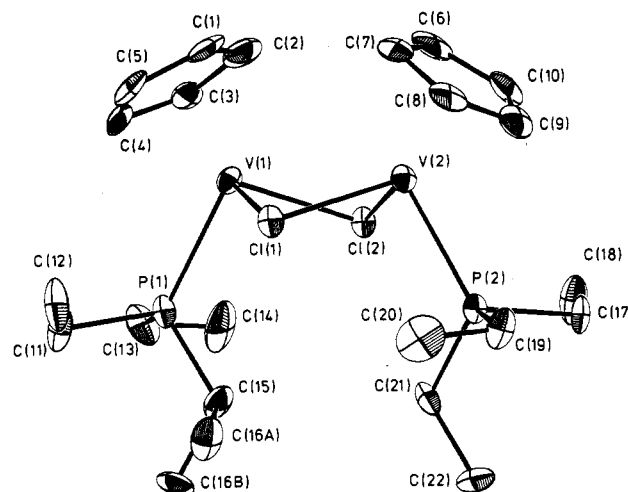


Figure 1. Molecular geometry and atomic numbering used for [CpVCl(PEt₃)₂]₂. Hydrogen atoms have been omitted for clarity. Hydrogen numbering is based on upon the numbering of the carbon atoms to which the hydrogen atoms are bound.

Table III. Interatomic Distances (Å) for [CpVCl(PEt₃)₂]₂

V(1)–V(2)	3.245 (3)	V(2)–C(8)	2.26 (1)
V(1)–Cl(1)	2.438 (3)	V(2)–C(9)	2.26 (1)
V(1)–Cl(2)	2.440 (3)	V(2)–C(10)	2.27 (1)
V(2)–Cl(1)	2.437 (3)	C(6)–C(7)	1.33 (2)
V(2)–Cl(2)	2.453 (3)	C(7)–C(8)	1.35 (2)
Cl(1)–Cl(2)	3.363 (4)	C(8)–C(9)	1.36 (2)
V(1)–P(1)	2.510 (4)	C(9)–C(10)	1.33 (2)
V(2)–P(2)	2.509 (4)	C(6)–C(10)	1.32 (2)
V(1)–M(1) ^a	1.934 (2)	P(1)–C(11)	1.83 (1)
V(1)–C(1)	2.24 (1)	P(1)–C(13)	1.86 (1)
V(1)–C(2)	2.24 (1)	P(1)–C(15)	1.80 (1)
V(1)–C(3)	2.24 (1)	C(11)–C(12)	1.50 (1)
V(1)–C(4)	2.27 (1)	C(13)–C(14)	1.46 (1)
V(1)–C(5)	2.26 (1)	C(15)–C(16A)	1.53 (1)
C(1)–C(2)	1.32 (2)	C(35)–C(16B)	1.53 (1)
C(2)–C(3)	1.29 (2)	P(2)–C(17)	1.84 (1)
C(3)–C(4)	1.39 (2)	P(2)–C(19)	1.80 (1)
C(4)–C(5)	1.35 (2)	P(2)–C(21)	1.79 (1)
C(1)–C(5)	1.34 (2)	C(17)–C(18)	1.52 (1)
V(2)–M(2) ^a	1.957 (2)	C(19)–C(20)	1.49 (1)
V(2)–C(6)	2.24 (1)	C(21)–C(22)	1.48 (1)
V(2)–C(7)	2.28 (1)		

^a Center of Cp ring.

Table IV. Bond Angles (deg) for [CpVCl(PEt₃)₂]₂

Cl(1)–V(1)–Cl(2)	87.2 (1)	V(2)–P(2)–C(21)	116.5 (3)
Cl(1)–V(1)–P(1)	94.1 (1)	C(17)–P(2)–C(19)	100.1 (5)
Cl(2)–V(1)–P(1)	94.8 (1)	C(17)–P(2)–C(21)	104.9 (5)
Cl(1)–V(2)–Cl(2)	86.9 (1)	C(19)–P(2)–C(21)	103.5 (5)
Cl(1)–V(2)–P(2)	96.3 (1)	P(1)–C(11)–C(12)	109.0 (8)
Cl(2)–V(2)–P(2)	91.5 (1)	P(1)–C(13)–C(14)	114.4 (8)
V(1)–Cl(1)–V(2)	83.5 (1)	P(1)–C(15)–C(16A)	127.1 (9)
V(1)–Cl(2)–V(2)	83.1 (1)	P(1)–C(15)–C(16B)	120.6 (9)
M(1) ^a –V(1)–Cl(1)	127.2 (1)	C(16A)–C(15)–C(16B)	71.9 (7)
M(1)–V(1)–Cl(2)	124.6 (1)	P(2)–C(17)–C(18)	114.0 (7)
M(1)–V(1)–P(1)	119.7 (1)	P(2)–C(19)–C(20)	114.5 (7)
M(2) ^a –V(2)–Cl(1)	126.9 (1)	P(2)–C(21)–C(22)	117.5 (7)
M(2)–V(2)–Cl(2)	128.8 (1)	C(1)–C(2)–C(3)	108 (1)
M(2)–V(2)–P(2)	116.8 (1)	C(2)–C(3)–C(4)	111 (1)
V(1)–P(1)–C(11)	118.1 (5)	C(3)–C(4)–C(5)	104 (1)
V(1)–P(1)–C(13)	115.7 (4)	C(4)–C(5)–C(1)	108 (1)
V(1)–P(1)–C(15)	116.2 (3)	C(5)–C(1)–C(2)	109 (1)
C(11)–P(1)–C(13)	96.0 (5)	C(6)–C(7)–C(8)	107 (1)
C(11)–P(1)–C(15)	103.0 (5)	C(7)–C(8)–C(9)	107 (1)
C(13)–P(1)–C(15)	105.0 (5)	C(8)–C(9)–C(10)	107 (1)
V(2)–P(2)–C(17)	112.9 (4)	C(9)–C(10)–C(1)	109 (1)
V(2)–P(2)–C(19)	117.0 (4)	C(30)–C(1)–C(2)	109 (1)

^a Center of Cp rings.

compound. Two bridging chlorine atoms are present. A surprising feature of the structure is the essential cisoid (2) arrangement

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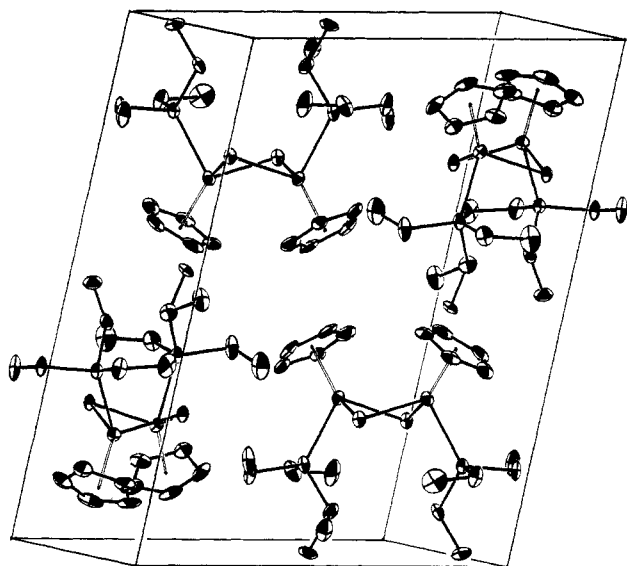


Figure 2. Unit cell packing of $[\text{CpVCl}(\text{PEt}_3)]_2$.

of the Cp and PEt_3 ligands around the V–V axis. The molecule possesses a noncrystallographic 2-fold axis that relates the two $\text{CpVCl}(\text{PEt}_3)$ units. These units are twisted relative to each other by an angle of about 4.5° . The V_2Cl_2 ring is puckered (roof shaped), and the angle between $\text{V}(1)\text{--Cl}(1)\text{--Cl}(2)$ and $\text{V}(2)\text{--Cl}(1)\text{--Cl}(2)$ is 132.9° . The V_2Cl_2 ring is symmetric with respect to the V–Cl–V angles ($83.5(1)^\circ$ and $83.1(1)^\circ$) and V– μ -Cl distances (average value 2.44 \AA). These V– μ -Cl distances are smaller than the V– μ -Cl distances in $[\text{V}_2\text{Cl}_3(\text{THF})_6]^+$ (average value 2.48 \AA)⁶ but still substantially longer than the terminal V–Cl distance in $\text{CpVCl}_2(\text{PMe}_3)_2$ (average value 2.40 \AA). The V–V distance is strongly reduced, due to the puckering of the V_2Cl_2 ring. For a planar ring with the same Cl–V–Cl angles and V– μ -Cl distances, the V–V distance would be 3.56 \AA . The reduced V–V distance amounts to in fact $3.245(3) \text{ \AA}$. However, this distance is still much longer than the single-bond distance of about 2.7 \AA . For comparison the V–V distance with three bridging Cl^- ions, in $[\text{V}_2\text{Cl}_3(\text{THF})_6]^+$ is $2.973(3) \text{ \AA}$.⁶ Puckering of the central ring is quite common in electron-rich dibridged dinuclear late-transition-metal complexes, e.g. $\text{Cp}_2\text{Ni}_2(\text{CO})_2^{12}$ or $\text{Co}_2(\text{CO})_8$.¹³ Steric repulsions between nonbridging ligands play a minor role in these types of compounds. In complexes of early transition metals usually more ligands are accumulated around the central atom, and therefore, steric influences probably generally prevent puckering; cf. $[\text{Cp}_2\text{Ti}(\mu\text{-Cl})_2]$ with a planar Ti_2Cl_2 ring.¹⁴ In the coordinatively unsaturated complex $[\text{CpV}(\mu\text{-Cl})(\text{PEt}_3)]_2$, it seems that steric interaction does not prevent an energetically favored puckering.⁸ It must be noted that the isoelectronic complex $[\text{CpCrCl}(\mu\text{-Cl})_2]$ was shown to have a planar Cr_2Cl_2 ring with a "transoid" arrangement of the ligands.¹⁵ This is possibly due to electronic repulsions of polarized terminal chlorine atoms. In contrast the complex $[\text{CpNb}(\text{CO})_2(\mu\text{-Cl})_2]$ shows puckering of the central ring¹⁶ and is described with a Nb–Nb single bond ($3.056(1) \text{ \AA}$).

The distances of the vanadium atoms to the centroids of the cyclopentadienyl ring show the normal values of 1.934 and 1.957 \AA (cf. 1.973 \AA in $\text{CpVCl}_2(\text{PMe}_3)_2$). The observed cyclopentadienyl C–C distances are substantially shortened due to the high thermal motion in these rings.⁸ The V–P distances of $2.510(4)$ and $2.509(4) \text{ \AA}$ are essentially the same as in $\text{CpVCl}_2(\text{PMe}_3)_2$ ($2.507(1)$ and $2.510(2) \text{ \AA}$). The PEt_3 conformation with non-equivalent C–P–C angles is more often observed for PEt_3 , e.g. in

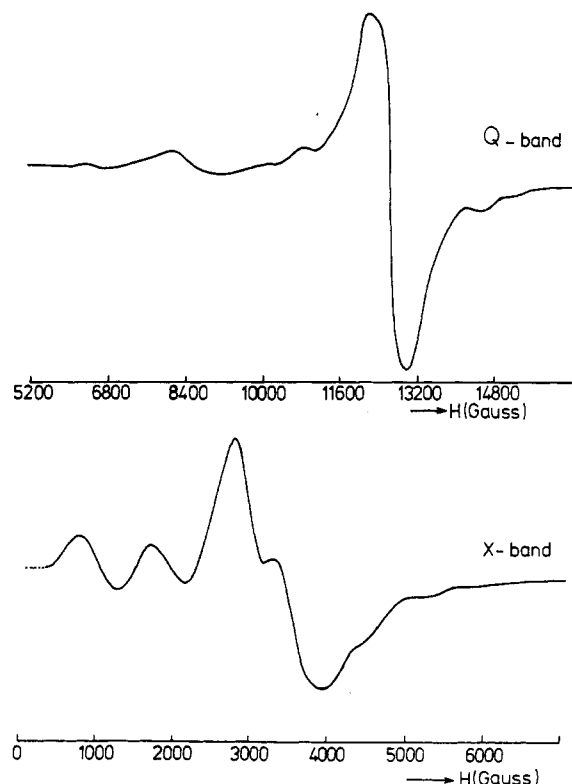


Figure 3. Room temperature X-band and Q-band ESR spectra of powdered $[\text{CpVCl}(\text{PEt}_3)]_2$, observed at microwave frequencies of 9.531 GHz and 35.028 GHz , respectively.

$\text{W}(\text{O})(\text{CHCMe}_3)\text{Cl}_2(\text{PEt}_3)$.¹⁷ In the solid-state molecule, dinuclear units of $\text{CpVCl}(\text{PEt}_3)_2$ are rather isolated from each other, as shown by the packing diagram depicted in Figure 2. Analysis of the intermolecular contacts showed that only van der Waals contacts are present.

ESR and Magnetic Susceptibility Measurements. Because dinuclear species of transition-metal ions with unpaired electrons quite often give rise to interesting magnetic properties, such as antiferromagnetism,^{18,19} ESR spectra of the title compound were recorded and its magnetic susceptibility was measured at several temperatures.

The room-temperature powder ESR spectrum is very interesting and at both X-band and Q-band frequencies a number of bands are observed. Spectra are redrawn in Figure 3. Interpretation of the powder spectra as two $S = 3/2$ spins or as an $S = 3$ spin appeared to be impossible. The lines are too broad, whereas cooling to liquid-nitrogen temperature reduced the intensity by a factor of about 50, indicative of thermal depopulation of an EPR active triplet or quintet state. For a full analysis of these interesting spectra, single-crystal analysis will be required. Similar studies on $\text{Cr}(\text{III}) S = 3/2$ dimers by others²⁰ have shown that such an analysis is very hard indeed. To check whether or not our broad lines were due to solid-state dipolar effects, we have recorded the spectra in frozen toluene at 77 K . However, a low-intensity signal is observed under these conditions that can be attributed to a monomeric impurity $\text{CpVCl}(\text{PEt}_3)_2$ formed from the dimer by reaction with PEt_3 ⁸ (liberated by partial hydrolysis or oxidation of the dimer on preparing the solution), with g values at 4.47 , 3.96 (with eight-line V hyperfine splitting of 22.5 G), and 3.41 . This signal is well in the range expected for a d^3 ion with a rhombic geometry.²⁰ Apparently, the dimer signal is too weak at low temperatures to be observed, suggesting that the ground state of

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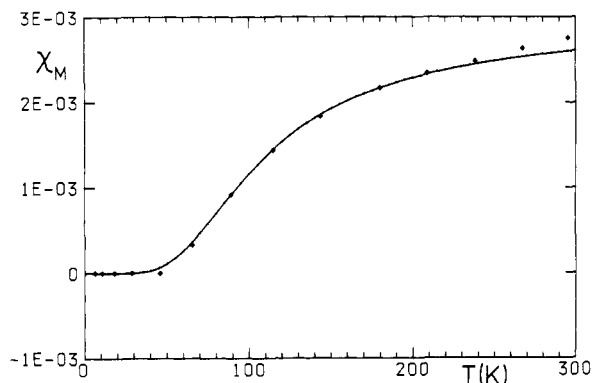
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Table V. Magnetic Susceptibility of (CpVClPEt₃)₂ at Various Temperatures

T, K	10 ³ χ _m , cgsu	10 ³ χ _M ^{cor, a} , cgsu	T, K	10 ³ χ _m , cgsu	10 ³ χ _M ^{cor, a} , cgsu
4.0	5.59	0	114.7	1.58	1.44
6.3	4.17	0	143.6	1.89	1.84
10.6	2.80	0	179.6	2.13	2.17
18.1	1.79	0	209.0	2.26	2.34
28.6	1.12	0	238.2	2.36	2.48
45.8	0.76	0	267.5	2.48	2.63
65.3	0.80	0.33	295.4	2.58	2.75
89.3	1.19	0.92			

^aSusceptibility of dimer after correction for diamagnetism (χ_{dia} = -0.40 × 10⁻³ cgsu) and 3.5% V³⁺(d²) impurity following χ_{para} = C/(T + θ) (θ = 16 K) above 50 K.

**Figure 4.** Plot of the magnetic susceptibility of [CpVCl(PEt₃)₂]₂ in the temperature range 4–300 K. The drawn curve has been calculated with $g = 2.00$ and $J = -109 \text{ cm}^{-1}$ (based on the formula given in the text).

the dimer is diamagnetic; i.e., the two ions should be coupled rather strongly and antiferromagnetically.

To study this exchange coupling in more detail, magnetic susceptibility measurements (Table V) were performed on the solid powder, down to 4 K. The resulting susceptibility curve, corrected for diamagnetism and a paramagnetic impurity, is given in Figure 4. The decrease with T of the susceptibility indeed confirms the antiferromagnetism, and the figure shows that at 77 K almost all magnetism has disappeared. The temperature-dependent part of the molar susceptibility for a d³–d³ dimer with equivalent metal centers was fitted with the expression²¹

$$\chi_{\text{mol}} = \frac{n\beta^2 g^2}{3kT} \frac{42 + 15 \exp(6x) + 3 \exp(10x)}{7 + 5 \exp(6x) + 3 \exp(10x) + \exp(12x)}$$

with $x = -J/kT$, where J is the exchange integral. A small correction was applied for a paramagnetic impurity (following a Curie–Weiss law). The best J value (drawn line in Figure 4) for [CpVCl(PEt₃)₂]₂ was -109 cm^{-1} and $g = 2.00$; for the related [CpVBr(PEt₃)₂]₂ we found $-J = 107 \text{ cm}^{-1}$ and $g = 2.00$. These values are substantially larger than those in [V₂(μ-Cl)₂(THF)₆]⁺ (-75 cm^{-1}), which is also a d³–d³ complex.⁶ Often a strong correlation is observed between the exchange integral $-J$ and the M–X–M bridging angle.^{18,19} However, in a d³ case the magnetic orbitals are pointing in between the ligands, in the case of octahedral geometry (such as in V₂Cl₃(THF)₆)⁺. In the present compounds, the geometry for each vanadium is trigonal, with two Cl ligands and one PEt₃ ligand occupying three sites of an octahedron and the Cp ring taking the other three sites. This results in a more distorted octahedron than in the case of the THF compound, and therefore more magnetic orbitals may point toward the (bridging) ligands and increase the σ exchange. In addition to these effects, exchange through π -bonding orbitals on Cl may influence the antiferromagnetism and also contribute to the increase in $-J$.

It is unlikely that direct exchange contributes to the observed magnetism, as the distance is very large.

Final Remarks

The results described above clearly indicate that the title compound is a strongly antiferromagnetically coupled dinuclear species, which is almost diamagnetic below liquid-nitrogen temperatures. The strong exchange can be understood on the basis of the molecular geometry, despite the long V–V distance. The roof shape of the V₂Cl₂ unit is a direct result of the cis arrangements imposed by them. In a related study,⁷ the chemical reactivity of this and other dinuclear V(II) compounds has been described.

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Supplementary Material Available: Table SII, anisotropic thermal parameters of non-hydrogen atoms, and Table SIII, fractional coordinates of the hydrogen atoms (2 pages); Table SI, calculated and observed structure factors (4 pages). Ordering information is given on any current masthead page.

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